TRANSIENT KINETIC STUDIES OF CHAR REACTIONS: GASIFICATION IN STEAM-ARGON MIXTURES

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I. INTRODUCTION.

In our laboratory we have been engaged in the study of the gasification behavior of chars using a transient kinetic approach. Previous work [1,2] concentrated on the development of the experimental techniques and carbon dioxide gasification. In the current communication we present some of our most recent data on the kinetic behavior of char gasification in steam-argon mixtures, and in so doing attempt to point out some of the significant advantages of transient techniques in studying the reactive behavior of chars, and in obtaining fundamental data.

The basis for this approach lies in the observation that the transient response of a reaction system to a perturbation in one or more of its state variables exhibits certain characteristics which are reflective of the "true" nature of the reaction mechanism under the appropriate experimental conditions. In comparison, steady-state rate measurements reveal relatively little concerning the detailed sequence of elementary steps that constitutes the "intrinsic" reaction mechanism. Thus, transient response data can be used in a qualitative sense to discriminate among competitive kinetic models. In addition, once an appropriate kinetic model has been identified, quantitative analysis of the transient data, using multiparameter estimation techniques, yields the model parameters. Moreover, the steady-state data, obtained at the end of each transient experiment, are available as well. The overall result of this approach is a more robust model of the reaction system under investigation.

II. EXPERIMENTAL.

A simplified schematic of the transient kinetic apparatus that was developed for the current experimental applications is presented in Figure 1. This system consists primarily of: (1) a continuous gas flow, fixed solids, Berty-type gradientless, isothermal reactor for carrying out the reaction under well-mixed conditions; (2) a solenoid/ control valve network for generating step function changes in feed composition; (3) a modulated, supersonic molecular beam mass spectrometer for monitoring the transient response of the composition of the gas phase at the reactor effluent; and (4) automated data logging and mass programming of the mass spectrometer utilizing a PDP 11/34-IBM 7406 device coupler combination. Additional system details and data on system performance establishing the "gradientless" nature of the reactor with respect to gas phase mixing and interphase heat and mass transport have been fully documented and are available elsewhere [3,4].

For the steam-argon gasification studies reported on here, an important modification to the original apparatus involved the addition of a steam generation system and a condenser/gas-liquid separator. The steam generator, which appears in schematic in Figure 1, consisted of a stainless steel cylindrical reservoir for feed water and a high temperature evaporator. From the reservoir, the liquid water was metered into an argon carrier stream. The water flow rate was measured with a digital flowmeter (American Flow Systems AQ 300; up to 20 cm^3/min). The combined water/argon flow was fed to an electric resistance-heated evaporator which produced superheated steam at the local thermodynamic conditions. All the upstream lines were heated and insulated to prevent steam condensation.

Various experimental considerations dictated that it was not desirable to attempt to maintain steam in the vapor phase downstream of the reactor up to the mass spectrometer sampling point. This would have involved heating and insulating the downstream lines, the adoption of another

method of flow rate measurement than the rotameters used in our previous studies, and would have created sampling problems due to the high fraction of water vapor expanding through the sampling orifice and condensing due to adiabatic cooling. Instead, therefore, it was decided to remove the bulk of the water immediately downstream of the reactor. This was accomplished using a specially-developed condenser. Insofar as the transient nature of the experiments is concerned, the introduction of any volume in the flow circuit of a magnitude comparable to that of the reactor would introduce an undesirable lag time in the system response, which if too large would tend to obfuscate the intrinsic transient response of the reactor. In addition, from an operational viewpoint it was essential to have whatever time lag that was ultimately introduced be invariant with the amount of collected liquid water in the condensate receiver. Of course, this could be accomplished by continuous removal of condensate; but this approach quickly leads to a complex control problem. Therefore, a simpler alternative approach was adopted. A baffle plate was installed at the bottom of the inlet dip tube to the condenser with circumferential slots for gas and condensate flow. In this manner, condensate could accumulate in the lower volume of the condenser, but the noncondensable fraction of the gas flow effectively "short-circuits" the condenser, immediately flowing to the outlet located in proximity, and thereby minimizing the imposed lag time. The effect of the condenser on the system transient response was measured by monitoring the exponential rise of an argon signal in the reactor effluent upon instantaneously switching this gas to the reactor feed line. Without the condenser in the flow circuit it was found, as previously [2], that the intrinsic time delay of the system was about 2 s. The effect of the condenser was the introduction of an additional additive lag time of 4 s, thereby making the new total system lag time about 6 s, which was found to be invariant with the liquid water level in the condensate receiver. This lag time proved to be of no practical consequence in the analysis of the data.

III. EXPERIMENTAL PROCEDURES.

The two gas phase product species that were monitored with the molecular beam mass spectrometer during the course of the transient experiments were CO ($m/e=28$) and H_2 ($m/e=2$). Automatic mass programming allowed alternate monitoring of these two species at a sampling frequency of about 1 Hz (0.5 Hz each), which was sufficient for the experiments conducted. (It is noted that the limiting factor in the current configuartion is not the mass programming, but rather the characteristic time of the lock-in amplifier which was used to extract the modulated portion of the signals.) Water, although also present in the sampled product gas, was not monitored, since the $m/e=18$ signal simply corresponded to the saturation vapor pressure of water at room temperature, the bulk of the water having been removed upstream in the condenser.

Since all the species of interest here are also normally present in the background of the oil diffusion-pumped mass spectrometer vacuum envelope, to a greater or lesser degree, it was important to insure that the mass spectrometer signals corresponded to the instantaneous composition of the gas phase at the sampling orifice, and were not being influenced primarily by the background. A modulated beam technique was employed for this purpose. The gas at the sampling point was expanded through a 25 μm diameter orifice into the first stage of a two-stage, differentially pumped vacuum system. In this stage (maintained ca. 1×10^{-4} torr) the expansion was cored by a 200 μm diameter, 60^0 conical skimmer, and admitted into the second, mass spectrometer stage (maintained ca. 5×10^{-7} torr). In this stage the beam was mechanically modulated with a 200Hz tuning fork chopper, and then passed through the ion source of the quadrupole mass spectrometer. The signal for each mass peak was then processed through a lock-in amplifier which extracted the rms value of the 200 Hz modulated signal only, thereby discriminating against the background contribution to the total signal. Mass discrimination in the sampled flow due to the jet expansion was found to be small [3], most probably due to sampling into the second stage while the beam was still relatively under-expanded.
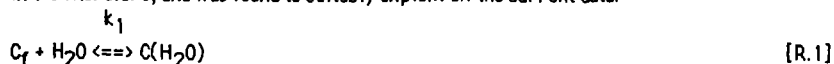
In order to insure that the CO and H_2 signals observed with the mass spectrometer could be entirely attributed to the steam-carbon reaction occurring within the reactor, a series of "blank" transient experiments was performed using steam-argon mixtures with non-porous glass beads in the solids basket in lieu of char. Two different reactor space times, 12 s and 18 s, were used. For each space time, experiments were performed at total pressures of 1.0, 1.3, and 2.0 MPa, and steam contents by volume of the steam-argon feed mixture of 50 and 70%. The char bed temperature in all cases was about 740 ^{0}C. No significant trace of either species was observed under these conditions. Thus, it was concluded that the CO and H_2 observed during the course of the transient gasification experiments originated from the steam-carbon reaction.

Another experimental concern related to the gas phase composition involved the water-gas shift reaction. This reaction is exothermic and thermodynamically favored under conditions of high steam partial pressure in the presence of CO to produce CO_2 and H_2. It has been reported that this reaction is approximately at equilibrium at temperatures of 800^{0}C and above in coal gasification systems [5]. However, it can be kinetically limited and, therefore, rather slow, unless it is appreciably catalyzed by impurities in the char. Insofar as the current experiments are concerned, its relative importance can be readily assessed by monitoring CO_2. Although we examined the m/e=44 signal during the course of our scoping studies, no appreciable modulated signal was observed. Thus, under the current experimental conditions, the practical effects of this reaction seem to be minimal.

Transient experiments were conducted by first establishing the reactor temperature and pressure under a continuous pure argon purge. The flowrates of the pure argon purge and steam-argon reactive mixture were matched using the upstream and downstream control valve system (cf. Figure 1) such that the space time of the reactor remained constant at reactor conditions upon switching the two flows. (In order to accomplish this, the measured liquid water flowrate was converted to equivalent steam flowrate at reactor conditions.) All these operations were accomplished without exposing the char to the steam-argon mixture by alternate switching between the purge and bypass lines. (The pressure drop across the reactor is negligible in comparison to that imposed by the solenoid/control valve system, and thus the open bypass line adequately models the reactor flow resistance.) Once the pressure, temperature, and flowrates were set in the preceding manner, the transient experiment was initiated by activating the solenoid valve system to switch between the two flows. Pre-set mass programming and automated data logging were initiated simultaneously with the inception of the experiment.

IV. KINETIC MODELING.

Various models have been proposed for the steam-carbon gasification system (e.g., see [6-10]). In the current studies, however, the complexity of the kinetic model required to explain the steam-char reaction was limited by the experimental conditions selected; i.e., only pure steam-argon feeds were used. Furthermore, for reactor space times of 12 to 18 s, the steam conversion never exceeded 10%. In addition, no significant amounts of methane or CO_2 were detected for the pressure and temperature ranges used. Under these conditions, the following mechanism was found to incorporate the basic features common to most of the models in the literature, and was found to suitably explain all the current data:

$$C_f + H_2O \overset{k_1}{\underset{k_{-1}}{\Longleftrightarrow}} C(H_2O) \qquad [R.1]$$

$$C(H_2O) + C_f \overset{k_2}{\longrightarrow} C(O) + C(H_2) \qquad [R.2]$$

$$C(O) \overset{k_3}{\longrightarrow} CO + C_f \qquad [R.3]$$

$$C(H_2) \xrightarrow{k_4} H_2 + C_f \qquad\qquad [R.4]$$

This mechanism is basically that of Curran et al. [10], except that reactions [R.2]-[R.4] are treated as irreversible; the latter two by virtue of the relatively low amounts of CO and H_2 produced in the reactor. Although this assumption seems to be quite good a priori for CO, it has been noted that under steady-state conditions, H_2 significantly inhibits the steam-char reaction, with a resultant multiplicative factor in the denominator of the Langmuir-Hinshelwood steady-state specific gasification rate expression of almost an order of magnitude greater than that for steam (e.g., see [6,8]). However, under the current transient experimental conditions with initially no H_2 in the reactor, and eventually very low amounts even at pseudo-steady-state, the sensitivity of the transient data to the rate of the reverse of reaction [R.4] seemed to be relatively low. Therefore, it was omitted from the current analysis on these grounds. It is noted, however, that it is certainly possible to determine this rate constant with the current techniques using either pure or high partial pressure H_2 feeds.

All the basic mechanisms represented in the literature employ a step like reaction [R.1] (i.e., steam adsorption); however, there is a range of treatment on subsequent details and rate-limiting steps. For example, Gadsby et al. [6] assumed essentially instantaneous decomposition of the carbon-steam surface complex to gaseous CO and H_2. Ergun [11] and Strickland-Constable [12] suggested this mechanism for H_2, but postulated a surface carbon-oxygen complex with an appreciable lifetime that eventually decomposes to yield gaseous CO. Long and Sykes [7] and Blackwood and McGrory [8] proposed decomposition to dual-site hydroxyl and hydrogen atom surface complexes simultaneously with steam adsorption (i.e., fast equilibration), followed by irreversible rearrangement to carbon-oxygen and carbon-hydrogen surface complexes. These differences are relatively indistinguishable from each other in the current data. Therefore, the combination of reactions [R.1] and [R.2] were selected as being most generally representative.

Once the model has been defined, the approach becomes quite similar to other general treatments of "lumped" transient kinetic models that have been presented in the literature (e.g., see [13,14]), and to our previous CO_2 gasification work [1,2]. The use of a "gradientless" reactor guarantees that the resultant mass balances are always ordinary differential equations (i.e., "lumped" parameter systems), although, as in the current case, they may be nonlinear. Basically, the transient continuity expressions for the various species involved in the reaction system, incorporating the rate expressions derived from the kinetic mechanism, comprise the set of ordinary differential equations which defines the model of the system.

Formulated in this fashion, the model employed to analyze our steam gasification data consisted of seven first order differential equations with a total of six parameters: C_{so} (the "effective" concentration of active sites; g mol/g mol carbon), k_1, k_{-1}, k_2, k_3, and k_4. The resultant system of equations is omitted from the current communication for the sake of brevity. Its derivation is relatively straightforward and is presented in reference [4].

V. PARAMETER ESTIMATION.

The multiparameter estimation algorithm employed in the analysis of the current data was patterned after a scheme outlined by Luus and Jaakola [15]. The Luus-Jaakola (LJ) scheme is a direct random search method combined with search space reduction. Basically, the procedure is as follows. An initial range is selected for each parameter, and a number of different parameter sets are then selected on a random basis. For each parameter set the model is solved numerically and an unweighted least squares objective function value, $\emptyset$, is determined using all the CO and H_2 partial pressure data over the entire course of the transient experiment; i.e.,

$$\emptyset = \sum_{i=1}^{2} \{ \sum_j (P_{i,j} - P^*_{i,j})^2 \}, \tag{1}$$

where the $P_{i,j}$ and the $P^*_{i,j}$ are the measured and predicted partial pressures, respectively. After an arbitrarily large number of parameter sets have been evaluated, a fraction of the "best" resultant cases (i.e., those with the lowest $\emptyset$ values) are then selected and the parameter ranges of these sets are scanned to define new reduced parameter ranges to be used for the next round of iteration. The entire procedure is then repeated until a pre-specified tolerance on the differential change in the objective function is met. The associated parameter set for the "best" value of $\emptyset$ after the last iteration is taken as the final optimum parameter set for the data.

The LJ method was applied to the steam gasification data on an experimental basis, with reasonable results, as part of an ongoing investigation on multiparameter regression schemes for transient kinetic data analysis [16]. Previously [1,2] we had used a Marquardt-type search scheme employing a Green's function method [17] for determining the first order gradients required for the technique. As for all such schemes, we found both advantages and disadvantages in using the LJ scheme. Perhaps its most obvious disadvantage lies in its inherent inability to converge to the optimum parameter set if it is inadvertently not included in the initial ranges of all the parameters. If the initial range is too large, the rate of region reduction can be drastically slower than if the range is capable of being more narrowly specified. Also, since a finite, albeit large, number of parameter sets are examined, there is always the possibility of missing the "true best" parameter set. Counterbalancing these debits is a potentially significant savings in computation time due to the absence of the requirement for evaluating first order gradients and, possibly, higher derivatives. Also, in reducing the parameter search space, the LJ method increases the probability of encountering a near-optimum parameter set, in comparison to totally random search methods. However, these arguments notwithstanding, our experience with the data considered here, suggests that a more effective method might involve a hybrid scheme wherein an LJ-type algorithm is used as the "front end" of an optimization procedure for reducing the parameter search space, with a more powerful local gradient technique, such as a Marquardt scheme, used to actually focus in on the optimum parameter set. Such a scheme is currently under consideration.

Typically, in the current application of the LJ method, the parameter ranges obtained after 11 iterations, using a 5% case reduction rate, were used as the initial ranges for the subsequent set of iterations. When the "best" value of $\emptyset$ did not change by more than 5%, the parameter set associated with this minimum value of the objective function was taken to be the optimum set. As an approximate average, about 25 overall iterations were sufficient to fit the experimental data with a good degree of accuracy.

VI. RESULTS AND DISCUSSION.

Two types of chars were studied in the current work: Fisher activated coconut char, and a char prepared from Darco lignite (PSOC 623) (800°C for 2 hr. in an inert atmosphere). Typical transient experiment results are presented in Figures 2 and 3. The six model parameters were determined for each transient experiment using the LJ algorithm as described above. The apparent activation energies for each parameter were then determined from Arrhenius plots of the parameter values. The resultant parameter expressions are summarized in Table I.

From the results in Table I it can be seen that the apparent activation energies are, on the whole, higher for the lignite than for the coconut char. However, the activation energies for k_1 are very nearly identical for the two chars, thereby implying that the mechanism for steam adsorption on the two chars is very similar. As in our previous CO_2 gasification studies, we found that the apparent activation energies of the effective active site concentrations were negative. This result, as previously, is attributed to the diminution of active sites via thermal annealing of the char upon heating [1,2,9,18,19,20]. Moreover, the C_{s0} parameter expression determined in the current steam gasification studies for the coconut char is very similar to that

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determined for the same char from previous CO_2 gasification studies: viz., $C_{so} = 1.7 \times 10^{-9}$ exp(+27000/RT) [1,2,3]. This result implies that virtually the same active carbon sites participate in steam and CO_2 gasification under the current experimental conditions. This is also direct evidence that the transient technique can yield good estimates of the effective active site concentrations of chars under actual gasification conditions.

It is interesting to note that C_{so} for the lignite char is comparable to that of the coconut char, even though their total surface areas are quite different (1038 m^2/g for the coconut char; and 24.7 m^2/g for the lignite char). However, C_{so} decreases more rapidly with temperature for the coconut char than for the lignite char, as evident from the relative magnitudes of their negative apparent activation energies. This result probably reflects the fact that the coconut char is "older" than the lignite char, and , thus, more graphitic in nature and more susceptible to thermal annealing, and, therefore, exhibits a stronger temperature behavior. Also, the fact that that disordered regions in char have bcen reported to react more rapidly than ordered regions [21], is consistent with the comparable C_{so} values of the two chars in spite of the significant difference in total surface areas.

Although values for all the rate constants determined in the current work are not available in the literature, comparisons can be made with steady-state Langmuir-Hinshelwood expression parameter values. Setting all the time derivatives equal to zero in the transient model and solving for the pseudo-steady-state specific gasification rate, W_{ss}, yields the following expression:

$$W_{ss} = K_1 P_w / [1 + K_2 P_w], \text{min}^{-1}, \tag{2}$$

where the correspondence between the new parameters and the rate constants is given by:

$$K_1 = k_1 k_2 C_{so}'[k_{-1} + k_2]; K_2 = k_1 [1 + k_2 (1/k_3 + 1/k_4)]/[k_{-1} + k_2] \tag{3}$$

A comparison of the parameter values calculated from these expressions with corresponding values given in the literature are presented in Table II. As can be seen, the comparison is fairly good. The primary source of the variability observed is most probably due to differences in the chars. For example, the total surface area of the coconut char used by Blackwood and McGrory [8] was reported as 46.5 m^2/g, in comparison to tha 1038 m^2/g for the activated coconut char used in the current work.

Pseudo-steady-state operation is attained at the end of each transient experiment corresponding the "leveling off" of the signal traces (e.g., after ca. 1.2 min). These data can also be analyzed in the usual steady-state fashion to show that they are consistent with traditional Langmuir-Hinshelwood kinetics. The steady-state expression given by Eq. (2) can be recast into the following form:

$$P_{w,ss}/W_{ss} = P_{w,ss} C_o RT/q P_{c,ss} = 1/K_1 + (K_2/K_1) P_{w,ss}, \tag{4}$$

where the subscript "ss" denotes steady-state values, $P_{c,ss}$ is the steady-state CO partial pressure determined from the data, q is the volumetric flowrate at the reactor exit, R is the universal gas constant, and T is the effluent gas temperature. Therefore, a plot of the lefthand side of Eq. (4) against $P_{w,ss}$ should be a straight line. One such plot for the coconut char data is presented in Figure 3; the linear behavior is quite evident.

VII. CONCLUDING REMARKS.

It has been shown that char gasification in steam-argon mixtures, under the current experimental conditions, is reasonably well represented by the transient kinetic model presented in this communication. Multiparameter analysis of the resultant transient kinetic data yielded separate Arrhenius temperature-dependent expressions for each of the model rate constants, as well as the effective active site concentrations for the two chars examined. Although corresponding rate constant expressions are not available for direct comparison, related kinetic parameters found in the literature agreed with the approprtate combinations of the current rate constant values.

The transient kinetic technique has been shown to be a valuable tool for examining char reaction mechanisms, and for determining rate parameters for direct use in modeling, design, and analysis of new or existing gasification and related systems. With automated data handling, the technique is capable of quickly and efficiently yielding a large amount of information concerning the reactivity and behavior of chars in various gaseous environments directly in a single type of experiment. The advantages of this technique over other more commonly accepted steady-state methods are significant.

ACKNOWLEDGEMENT

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Table I.

Model parameter values* obtained with the Luus-Jaakola search scheme for steam gasification of lignite and coconut char.

Values for Darco lignite char (PSOC 623):

$C_{so} = 1.6 \times 10^{-6} \exp(+13646/RT)$, g mol/g mol C

$k_1 = 4.86 \times 10^9 \exp(-42286/RT)$, min^{-1} atm^{-1}

$k_{-1} = 2.65 \times 10^{10} \exp(-51341/RT)$, min^{-1}

$k_2 = 9.32 \times 10^7 \exp(-33840/RT)$, min^{-1}

$k_3 = 4.21 \times 10^9 \exp(-42075/RT)$, min^{-1}

$k_4 = 5.07 \times 10^{10} \exp(-47262/RT)$, min^{-1}

Values for Fisher activated coconut char:

$C_{so} = 2.21 \times 10^{-8} \exp(+23592/RT)$, g mol/g mol C

$k_1 = 1.41 \times 10^{10} \exp(-45183/RT)$, min^{-1} atm^{-1}

$k_{-1} = 1.04 \times 10^7 \exp(-35233/RT)$, min^{-1}

$k_2 = 9.67 \times 10^4 \exp(-19448/RT)$, min^{-1}

$k_3 = 1.20 \times 10^6 \exp(-25995/RT)$, min^{-1}

$k_4 = 2.04 \times 10^6 \exp(-25867/RT)$, min^{-1}

*All activation energies are given in cal/g mol.

Table II.

Comparison of kinetic parameters from different studies with coconut char.

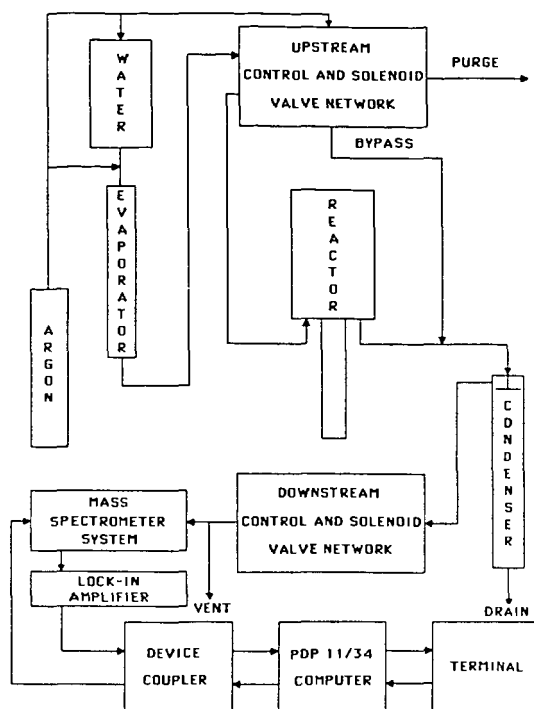| Temperature (K)	973.2	1023.2	1063.2
1. Current Work			
$K_1 C_{so} \times 10^4$, [min^{-1} atm^{-1} g mol/g C]	3.6	6.1	8.9
K_2, [atm^{-1}]	1.1	1.8	2.7
2. Gadsby et al. [6]			
$K_1 C_{so} \times 10^4$, [min^{-1} atm^{-1} g mol/g C] [min^{-1} atm^{-1} g mol/g C]	3.6	–	–
K_2, [atm^{-1}]	1.0	–	–
3. Long and Sykes [7]			
$K_1 C_{so} \times 10^4$, [min^{-1} atm^{-1} g mol/g C] [min^{-1} atm^{-1} g mol/g C]	1.6	7.8	25.0
K_2, [atm^{-1}]	0.97	1.61	2.33
4. Blackwood and McGrory [8]			
$K_1 C_{so} \times 10^4$, [min^{-1} atm^{-1} g mol/g C]	–	0.36	1.25
K_2, [atm^{-1}]	–	0.06	0.09

Figure 1. Schematic of experimental system.

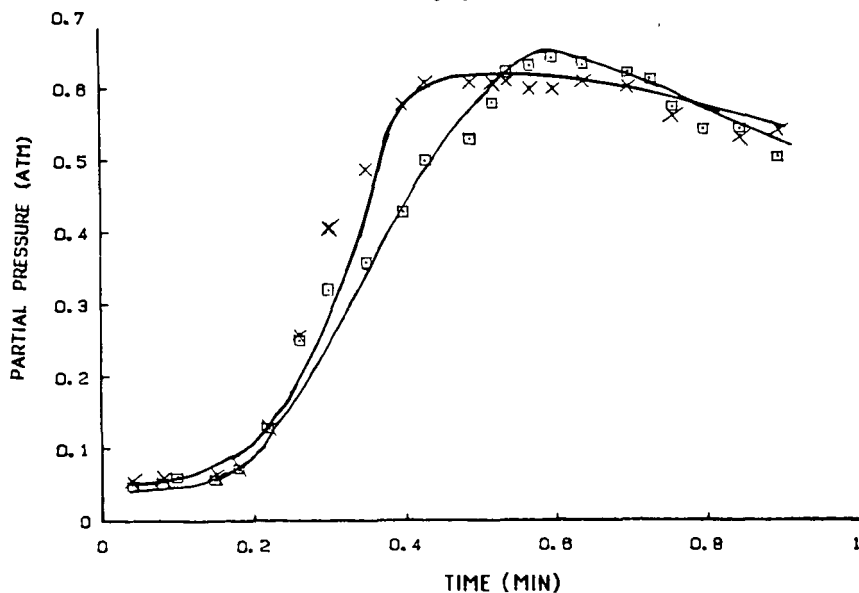EXPERIMENTAL RESPONSE OF [CO] AND [H2] VERSUS MODEL PREDICTION

Figure 2. Experimental transient responses of CO and H_2 versus model predictions for steam gasification of Fisher activated coconut char (2.135 g mol of char; T_{bed}=757°C, P_{total}=13.6 atm; P_{steam}=7.5 atm).
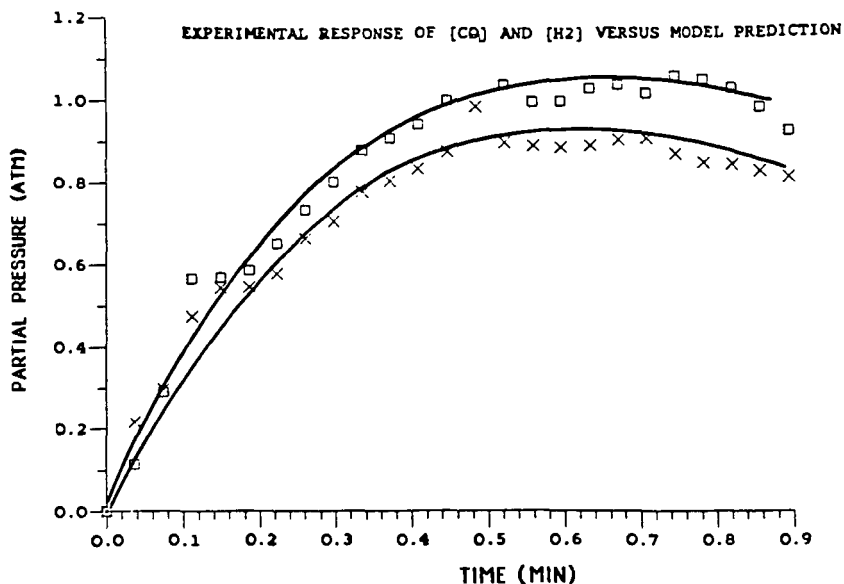
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Figure 3. Experimental transient responses of CO and H_2 versus model predictions for steam gasification of Darco lignite (PSOC 623) char (2.903 g mol of char; T_{bed}=765^{0}C, P_{total} =23.4 atm; P_{steam} =14 atm).
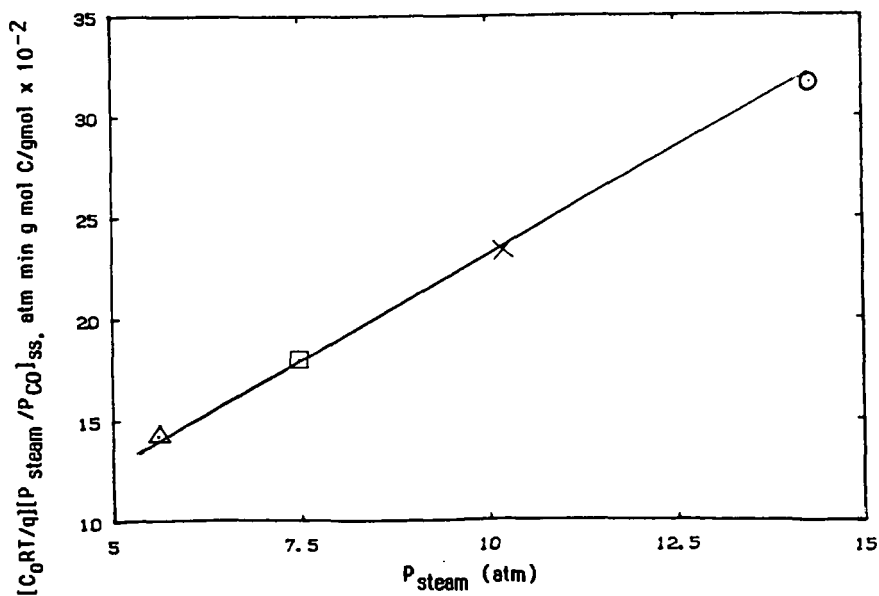

Figure 4. Pseudo-steady-state steam gasification rate data for Fisher activated coconut char (T_{gas}=1058 K, 2.135 g mol of char).